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RESEARCH AND DEVELOPMENT STUDY
RELATED TO THE SYNTHESIS OF
FORMALDEHYDE FROM CO₂ AND H₂

GARD Project 1416

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SYNTHESIS OF FORMALDEHYDE

Introduction

This report summarizes the activities of the General American Research Division during February through April, 1967 on Contract NAS2-3889, Synthesis of Formaldehyde. The activities during this quarter were concerned with (1) oxidation of methane to formaldehyde using nitrogen oxide gaseous catalysts, alone and in the presence of alkali tetraborates, (2) oxidation of methane to formaldehyde using ozonized oxygen in the presence of barium peroxide promoted with a silver oxide catalyst, and a nickel-tungsten catalyst, and (3) a literature search and study concerning the production of methanol from CO₂ under atmospheric pressure.

The highest formaldehyde yields obtained so far from the oxidation of methane in the presence of gaseous nitrogen oxide catalysts were 1.35% in single pass reactors and 6.4% in a recycle system, based on methane in the feed gas. The reaction zones of these reactors were filled with 6 mm porcelain Berl saddles coated with potassium tetraborate. Empty reactors, even when coated with potassium tetraborate, produced only up to 0.9% formaldehyde yields.

The production of formaldehyde by the oxidation of methane with ozonized oxygen in the presence of a catalyst consisting of BaO₂ activated with 0.5% Ag₂O and 1% Na₂O₂ was investigated under varying conditions. In spite of numerous attempts, no more than trace amounts of formaldehyde could be produced using this catalyst. A nickel-tungsten catalyst produced a 0.3% yield.

Thermodynamic calculations and published experimental evidence indicate that methanol can be produced at atmospheric pressure in realistic yields, e.g. 5 to 20%, only at temperatures lower than 200°F. The feasibility of methods

involving catalysts or electrical discharge techniques will be considered and evaluated.

1. Partial Oxidation of Methane Using Nitrogen Oxide Catalysts

The use of nitrogen oxides as homogeneous gas phase catalysts for the partial oxidation of methane to formaldehyde has been reported by several investigators, primarily Germans and Russians. Generally, the reported yields of formaldehyde based on methane in the feed gas are low and range from about 1% to 2.8% in single pass reactors. The total yield can be increased by employing either several reactors connected in series or a recirculating system. Enikolopyan et al¹ have obtained yields of formaldehyde reaching 7.5% of methane in the feed using three consecutive reactors and up to 21% in a recirculating system, with a 10-fold recycling of the gases. A German patent issued to Guttehofnungshütte² claims a 65% yield of formaldehyde using a 28-fold recirculation of the gas mixture.

The Guttehofnungshütte process utilizing nitrogen oxide catalyst is reported as being used on a pilot plant scale in Rumania.³ A gas mixture consisting of 18% CH₄, 9% O₂, 68% N₂, 3% CO, 1.6% CO₂ and containing about 0.08% NO is recirculated through a tubular reactor at 600 - 620°C and a contact time of 0.15 - 0.2 seconds. About 8 - 9.5% of the methane is converted into formaldehyde. A similar process is reported as being used in the USSR producing 3000 tons/year of formaldehyde.⁴

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1. N. S. Enikolopyan, N. A. Kleimenov, L. V. Karmilova, A. M. Markevich, and A. B. Nalbandyan, Zhur. Prikl. Khim. 32, 1132 (1959).
 2. Ger. Pat. No. 819,990, July 8, 1949.
 3. FIAT Report No. 1085, March 13, 1947.
 4. S. F. Gudkov, Gazovaya Promischlennost 8 (9), 44 (1963).

There is no universal agreement on the best feed gas composition or the reaction temperature. The reported feed gas compositions range from methane:air ratios of 3.7:1 to 1:3 and methane:oxygen ratios of 3:1 to 1:1. The best reaction temperatures reported in the literature range from 700°F to about 1200°F. Most of the reports, however, agree that nitrogen oxide concentrations of 0.08-0.25% are sufficient to produce good yields of formaldehyde. Although some processes use empty heated reaction vessels, there seems to be sufficient indication that when the reaction zone is packed with supports coated with alkali tetraborates, the reaction becomes more reproducible and results in higher formaldehyde yields.

The oxidation of methane using nitrogen oxide catalysts has been investigated in our tests using both single pass and recirculating systems. In both instances, the feed gas was prepared by mixing metered amounts of C.P. grade methane with dry oxygen to which known amounts of nitrogen oxides were added. The pressure in the reactor system was 3 - 5 mm Hg above atmospheric.

1.1 Single Pass Reactors

Nitrogen oxide catalysts have been investigated in single pass reactors at temperatures ranging from 600°F to 1200°F and space velocities up to 3000 hr⁻¹. The feed gas mixture consisted of 53 - 60% methane and 47 - 40% oxygen by volume and contained from 0.2 to 1.9% of nitrogen oxides. Initially, nitrogen dioxide was used; however, it tends to condense in the gas lines at room temperature causing difficulties in flow control. All of the other experiments were performed using nitric oxide which was injected into the oxygen stream where it reacted to give a mixture of NO and NO₂.

The reactors used in these tests were either 23 mm I.D. or 17 mm I.D. Vycor tubes, 18 inches long. The center of the reactor tube was surrounded by a tubular resistance heater providing a 4" long heated zone. The temperature was measured by a chromel-alumel thermocouple inserted into a thermocouple well situated in the longitudinal center of the reactor tube. The gases, methane and oxygen, were metered separately and then mixed before entering the reactor. The product was passed through a fritted glass disperser and bubbled through a known volume of water which dissolved the formaldehyde formed during the experiment. After each test a sample of the water solution was analyzed with a gas chromatograph using a Porapak Column. The yields of formaldehyde were calculated from the amounts of formaldehyde found in the water solution and the volumes of methane used in the feed gas.

With an empty, uncoated reactor, the best results were obtained at 1200°F, with 1.4% nitric oxide; the yield of formaldehyde reached 0.9% of the methane in the feed gas. Unfortunately, the presence of nitrogen oxides caused frequent flashes and rapid combustion of methane inside the reactor at 1000°F or higher. In an attempt to reduce this flashing, the reaction tube was coated with an alkali tetraborate film; however, such coating neither reduced the flashing nor increased the formaldehyde yield.

Next, experiments were performed in reactors with the heated zone filled with solid support material which was coated with potassium tetraborate. Activated alumina, high surface silica boiling chips, 6 - 12 mesh silica gel, and 6 mm porcelain Berl saddles were used for support materials. They were coated with potassium tetraborate by soaking in a 3 - 5% solution,

predrying in air, and drying in an oven at 110°C. Activated alumina produced no formaldehyde at all, while silica gel and silica boiling chips gave up to 0.25% yields. The procelain Berl saddles coated with potassium tetraborate produced the best results giving up to 1.35% formaldehyde per single pass at 1,000°F and nitrogen oxide concentrations of 0.2 - 0.4%.

Formaldehyde yields higher than 1% were obtained in many runs with space velocities ranging from 900 hr⁻¹ to 3000 hr⁻¹; however, the reproducibility of results in this region seems to be insufficient to obtain an exact relationship relating the formaldehyde yields to the space velocity. It appears that local overheatings have been occurring which caused a sudden increase in the CO formation with accompanying heat release and uncontrolled jumps in temperature.

1.2 Recycling System

A recycling system was built using a 23 mm I.D. Vycor reactor tube. A four-inch long heated reaction zone was filled with 6 mm procelain Berl saddles coated with potassium tetraborate. The gas was recirculated by a diaphragm pump; the recirculating flow velocity could be varied independently of other variables. Formaldehyde was removed from the reaction product by absorbing it in water in a gas wash bottle connected to the exit end of the reactor between the reactor and the recycle pump. A portion of the product gas washed free of formaldehyde was vented; an equivalent amount of gas mixture consisting of 60% CH₄ and 40% O₂ with 0.4 - 1.0% NO was added to the recycle system upstream of the reactor.

The highest formaldehyde yields obtained in this recycle system reached 6.4% based on methane fed into the system with a twenty-fold recycle ratio; this total yield is equivalent to only 0.32% per pass.

2. Oxidation of Methane Using Ozonized Oxygen

The oxidation of methane to formaldehyde with ozonized oxygen is based on the so-called Hibernia process³ which is reported to be capable of converting methane to formaldehyde in good yields. In this process, oxygen or air is passed through a catalyst bed maintained at 100° - 300°C. The catalyst consists of barium peroxide powder activated either by addition of 0.5% Ag₂O or 1% Na₂O₂ and 0.5% Ag₂O. This mixture is applied on unglazed porcelain chips, approximately 4 - 10 mesh, by rolling slightly wet chips in the catalyst powder. The resultant catalyst contains about 10% by weight of BaO₂.

Originally, this catalyst was used with coke oven gas with a typical analysis of 70% CH₄, 12% N₂, 11% CO, 4% H₂, and 3% C₂H₄. The ratios of the methane containing gas to the ozonized oxygen ranged from 60:40 to 70:30 and the reported yields of formaldehyde per pass reached up to 25% of the methane in the gas. When pure methane was used, the yield of formaldehyde decreased considerably; however, a yield of 9.7% per pass has been reported using 99.8% pure methane in a 70:30 ratio with ozonized oxygen and catalyst bed temperature of 103°C.⁵

A series of experiments has been performed to ascertain the workability of the Hibernia process using ozonized oxygen. Unfortunately, using BaO₂

5. Ger. Pat. No. 886,901, Aug. 17, 1953.

based catalyst, all attempts resulted in very low yields of formaldehyde. Somewhat better results were obtained with a commercial catalyst containing 6% nickel and 19% tungsten on alumina, where formaldehyde yields of up to 0.27% based on the methane in the gas were obtained.

2.1 Experimental Arrangement and Techniques

Two different catalyst bed arrangements were used in this investigation. In the first arrangement, the entire gas mixture was passed through a vertical catalyst bed which was retained on a stainless steel screen, and heated by an electric heater surrounding the reaction tube at the height of the catalyst bed. In the second, the catalyst was contained in a fused silica boat resting in a horizontal glass tube with the gas stream passing over the catalyst. In this arrangement, the reaction gases and the products were heated less, and decomposition of ozone was decreased; this configuration also simplifies investigation of catalysts in powder form. The ozonized oxygen and the methane were brought into the reaction tube by separate lines and were mixed inside of the tube. A similar gas inlet design was used in the Hibernia process to prevent the accumulation of small amounts of unsaturated hydrocarbons which can react explosively with ozone. No explosions have occurred during this work. The ends of the reactor were closed with silicone stoppers which were sealed to the glass reactor with Silastic 732 RTV adhesive. Silicone stoppers were found satisfactory and impervious to ozone, while ordinary black rubber was attacked severely.

The ozone used for testing was generated by a Type O3C1 ozonator manufactured by the Ozone Research and Equipment Corp., Phoenix, Arizona. This ozonator employs a high-voltage silent discharge to convert oxygen mixtures

containing up to 7 weight percent of O_3 . The concentration of ozone was determined by a standard thiosulfate, tri-iodide method. The methane used was a CP grade obtained from the Matheson Company.

2.2 Catalyst Materials

The first catalyst material used with ozone, based on the Hibernia process, was prepared by mixing dry powder materials to give a mixture containing 98.5% BaO_2 , 1% Na_2O_2 , and 0.5% Ag_2O by weight. This material was tested in the following four configurations:

1. Catalyst powder was mixed intimately with a fine porcelain powder in a 1:10 weight ratio and pressed into 1/4" tablets.
2. Porcelain chips were slightly moistened and sprayed with a light coating of the catalyst powder, providing a minimal thickness of catalyst.
3. Moistened porcelain chips were mixed with the catalyst powder so that the final product consisted of porcelain chips coated with a thick coating of the catalyst powder.
4. Pure catalyst powder was supported in a fused silica boat.

A second material was also tested; this was a commercial catalyst containing 6% nickel and 19% tungsten on an alumina carrier. This catalyst showed better than average yields of formaldehyde in previous screening of solid catalysts and it appeared as a likely material to be tested in the presence of ozonized oxygen. (Yield = 0.4% at 1200°F, 600 cc/min. total flow, 53% CH_4 , Test No. O-72.)

2.3 Results

A total of 63 tests were performed using mixtures containing 47% of ozonized oxygen and 53% of methane as feed material. The temperature of these tests ranged from 220°F to 1000°F; the flow rates of the gas mixture were varied from 15 cc/min. to 920 cc./min. (i.e. approximate space velocities from 9 hr⁻¹ to 190 hr⁻¹); and the ozone concentration in the oxygen ranged from 0.1% to 3% by volume.

In all the tests, the barium peroxide - silver oxide - sodium peroxide catalyst produced no more than trace amounts of formaldehyde. The Ni-W catalyst, which was tested only in a silica boat in the horizontal reactor, produced up to 0.27% yields of formaldehyde based on the methane at 600°F, 920 cc/min. total flow, and 1% O₃ in oxygen. (Test No. 0-176).

3. Synthesis of Methanol from Carbon Dioxide

In the investigation of the synthesis of formaldehyde from carbon dioxide, the possibility of obtaining methanol from carbon dioxide and hydrogen in good yields is of particular interest since the methanol formed can be easily converted to formaldehyde. The reactions of carbon monoxide with hydrogen have been studied and reported extensively by many investigators; however, literature on the reaction of carbon dioxide and hydrogen to form methanol is relatively scarce.

The overall reaction of methanol formation from carbon dioxide and hydrogen can be expressed as:



This reaction is exothermic; therefore, an increase in the reaction temperature decreases the equilibrium constant and diminishes the yield of methanol. The free energy of reaction (1) has been evaluated⁶ and can be expressed by

$$\Delta F_T^\circ = - 8,177 + 13.922T \ln T - 0.0047036T^2 - 0.8507 \times 10^{-6}T^3 + 0.32825 \times 10^{-9}T^4 - 47.32T \text{ cal./mole}, \quad (2)$$

where T is the absolute temperature in degrees Kelvin.

The reaction of CO₂ with H₂ to give methanol is thought to proceed in two stages:



The rates of reactions (3) and (4) are not the same and each depend on the composition of the reacting gases, temperature, pressure, and space velocity. However, Karpov⁷ showed that the optimum temperature for CO₂ conversion to CO is the same as for the methanol synthesis from CO and H₂ using the same catalysts; this temperature ranged from 600 to 650°F.

The equilibrium constants for these three reactions are shown in Figure 1, where log K is plotted vs. 1/T at one atmosphere. Although the equilibrium for the methanol formation from CO₂ (and also from CO) is more favorable at low temperatures, no catalyst has been found which is capable of producing methanol in good yields at temperatures below 440°F. In fact, all practical methanol processes run at temperatures of about 600°F. Unfortunately, the equilibrium concentration of methanol under 1 atmosphere pressure and at 440°F

6. K.A. Kobe et al. Petroleum Refiner 28 (11), 127 (1949); 29 (9), 135 (1950); 37 (7), 125 (1958).

7. A. Z. Karpov, Prom. Org. Khim. 6 (10), 574 (1939).

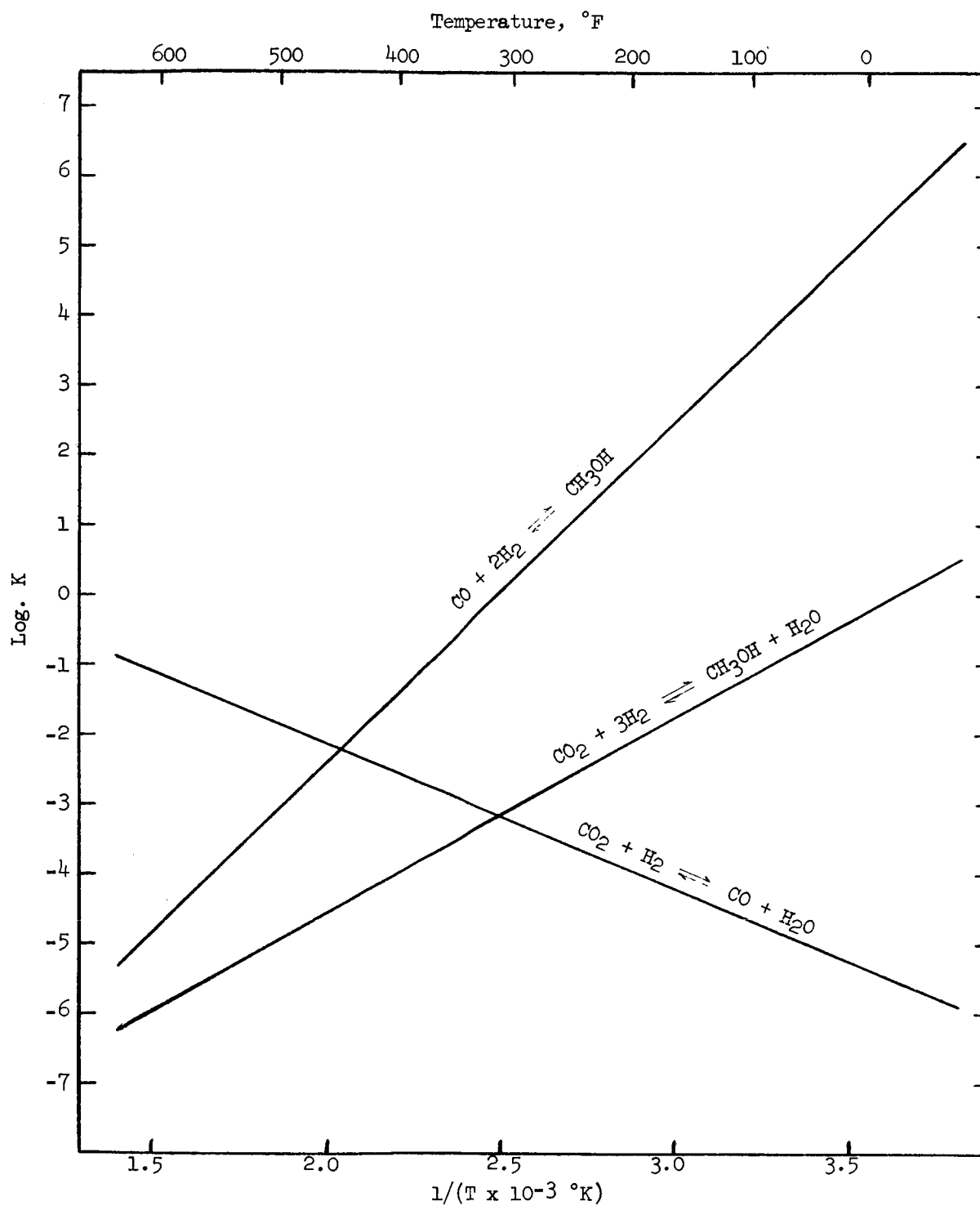


Figure 1. EQUILIBRIUM OF METHANOL FORMATION.

approximates 0.7% for reactions starting with CO_2 and 0.2% for CO.

Because of the unfavorable equilibrium at temperatures necessary to obtain satisfactory reaction velocities, at one atmosphere, practical yields of methanol either from CO_2 or CO can be obtained only under elevated pressures where the equilibrium becomes more favorable to methanol formation. An example of the influence of pressure on the formation of methanol is shown in Table 1, which is taken from Ipatieff and Monroe⁸. They investigated copper-alumina catalysts under various temperatures, pressures, and $\text{CO}_2:\text{H}_2$ ratios. At optimum temperatures (510 - 540°F), the conversion of CO_2 to methanol was possible only under high pressures. Various other catalysts have been investigated; however, the literature does not indicate any catalyst

Table 1. METHANOL FORMATION UNDER VARIOUS PRESSURES.

Temp., °F	$\text{CO}_2:\text{H}_2$ Ratio	Pressure, atm.	% CO_2 Converted to CH_3OH
540	1:4.3	409	94.3
510	1:4.3	235	27.1
510	1:5.3	117	12.6

suitable for methanol production from CO_2 at one atmosphere. Pospeshov⁹ found that some methanol can be obtained under 10 atm. but at least 30 - 40 atm. are necessary for practical yields with Cu, ZnO, and Cr_2O_3 catalysts. Dolgov¹⁰, after consideration of the whole problem of methanol production,

8. V. N. Ipatieff and G. S. Monroe, J. Am. Chem. Soc. 67, 2168 (1945).

9. D. A. Pospeshov, Zh. Khim. Prom. 14, 24 (1937).

10. B. N. Dolgov, Zh. Khim. Prom. 8, 457 (1931).

came to the conclusion that production of methanol from carbon oxides becomes practical only above approximately 68 atmospheres.

Although the equilibrium constant is higher when CO is used as the starting material, the conversion to methanol at one atmosphere is practically impossible. The effect of pressure on the reaction of CO and H₂ to give methanol has been considered by Ewell¹¹. The results of these calculations for a practically useful temperature of 570°F are given in Table 2 and indicate that elevated pressures are necessary to obtain any appreciable

Table 2. EFFECT OF PRESSURE ON CH₃OH FORMATION FROM CO.

Temp., °F	Pressure, atm.	CO:H ₂ Ratio	% Conversion to CH ₃ OH
570	10	1:2	0.4
570	25	1:2	1.7
570	50	1:2	8.0
570	100	1:2	24.2
570	200	1:2	48.7
570	300	1:2	62.3

amounts of methanol. In practice, methanol plants using CO operate at temperatures between 570°F and 700°F and pressures of 270 - 350 atm. The usual conversion under these conditions amounts to 12 - 15% per pass.

A large number of metals, metal oxides, and their mixtures has been claimed as catalysts for the production of methanol from carbon oxides.

11. R. H. Ewell, Ind. Eng. Chem. 32, 147 (1940).

Beckman, Morrell, and Egloff¹², for instance, tabulate catalysts for methanol synthesis on pages 685 to 689; similar lists are given in other reviews and books. The most active catalysts, however, are either zinc oxides or copper and copper oxides, both usually containing chromium oxide additives. The copper based catalysts are active at lower temperatures ($\sim 400^{\circ}\text{F}$); however, they are very sensitive to poisoning by sulfur compounds. Zinc oxide catalysts are less susceptible to poisoning but show good activity only at approximately 650°F .

Both the theoretical considerations and the experimental evidence available in the literature indicate that the formation of methanol directly from CO_2 or CO is impractical under atmospheric pressure at temperatures necessary with the presently used catalysts. Thermodynamic equilibrium calculations give a maximum conversion to methanol reaching only 0.7% of the CO_2 at 440°F , which is considered the lowest practical temperature. On the other hand, equilibrium conversion of CO_2 gives approximately 3.5% methanol at 212°F and 23% at room temperature (68°F) and atmospheric pressure. It is clear that the production of methanol from CO_2 under atmospheric pressure is possible only with methods providing higher reaction velocities at low temperatures. Two areas of investigation seem to be appropriate. First, catalysts which show some activity, although insufficient for commercial purposes, should be re-examined at low temperatures. Second, the possibility of reacting CO_2 and H_2 mixtures in the presence of electrical discharges should be investigated. It is known that in some cases the kinetics are greatly enhanced by silent

12. S. Beckman, J. C. Morrell, and G. Egloff, "Catalysis", Rheinhold Publishing Corporation, New York, N.Y., 1940.

electrical discharges; also, it has been reported in the literature that mixtures of CO_2 and H_2 give a mixture of oxygenated products in electrical discharges.

4. Future Activities

The conversion of methane to formaldehyde using nitrogen oxide gaseous catalysts will be further studied in both single pass and recirculating systems. Particular attention will be paid to establishing the exact and reproducible optimum conditions.

Use of ozonized oxygen in conjunction with other solid catalysts will be investigated in single pass and recycling systems.

Experiments for the separation and purification of formaldehyde from the reaction gases in the form of solid paraformaldehyde will be undertaken, initially using vapors in equilibrium with solid paraformaldehyde at different temperatures, and then actual reaction gases.

Investigation of possible processes for methanol production from carbon dioxide will be continued, with efforts directed to reported methods showing promise at low temperatures and atmospheric pressure; the feasibility of various catalysts and electrical discharge techniques will be considered and evaluated.